CHARACTERIZATION OF HIGH BOILING FISCHER-TROPSCH LIQUIDS

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INTRODUCTION

Fischer-Tropsch liquids obtained through the indirect liquefaction of coal via synthesis gas ($CO+H_2$) are expected to become an important source of fuel during the next several decades. Their commercial feasibility has already been demonstrated (1).

The hydrocarbon products from the Fischer-Tropsch process range from methane to high molecular weight compounds. In addition, relatively large amounts of oxygenates are produced. The quality of the gasoline product is such that extensive upgrading is required to produce stable, high octane motor fuels. Synthesis gas has been converted to high octane gasoline by a combination of Fischer-Tropsch synthesis followed by product upgrading with a ZSM-5 class catalyst. The application of ZSM-5 class catalyst to the production of high octane gasoline from methanol has already been demonstrated (2-4).

In conjunction with process development for the conversion of synthesis gas to high octane gasoline analytical methods are being developed to characterize in considerable detail the hydrocarbons and oxygenates in Fischer-Tropsch stage one effluent prior to their passage over a reactor with ZSM-5 class catalyst. These techniques will enable the effects of process variables on the composition of stage one products to be measured and subsequent effects of variations in Fischer-Tropsch composition on ZSM-5 catalysis to be defined.

Published Fischer-Tropsch analytical methods (5-11) have dealt mainly with relatively low molecular weight components produced during Fischer-Tropsch catalyst studies with little emphasis on the higher boiling hydrocarbons and oxygenates which may be produced in large scale reactors.

In this paper, gas and preparative liquid chromatographic methods for the characterization of Fischer-Tropsch hydrocarbons and oxygenates boiling above 170°C (C10+) are presented.

EXPERIMENTAL

Materials. Fischer-Tropsch samples obtained under various process conditions were studies in detail. All three samples represented mostly components boiling above 170°C (C10+).

Separation Scheme. The separation scheme (Figure 1) devised to isolate and characterize the various compound classes found in Fischer-Tropsch liquids consisted of preparative low pressure liquid chromatography (LC) and gas chromatography. Total hydrocarbons isolated by silica LC were resolved into paraffins and olefins by argentation liquid chromatography as previously described elsewhere (12).

Silica Low Pressure Liquid Chromatography. The LC system consisted of a Waters 6000 pump (Waters Associates, Milford, Mass.)

and a Rheodyne 70-10 valve containing a 10 ml sampling loop. Solvents were distilled in glass (Burdick & Jackson, Muskegeon, Michigan). A 30cm x 15mm i.d. glass column was packed with 20-44 micron Bio-Sil silica gel (Bio-Rad, Richmond, Calif.) activated in air at 150 C for 12 hours.

2.7 gms of the Sample A Fischer-Tropsch liquid was injected directly onto the liquid chromatographic column. Samples B and C contained an insoluble high molecular weight wax which was removed prior to liquid chromatographic analysis to prevent plugging of the injection valve and column. Soluble hydrocarbons and oxygenates were extracted from this insoluble wax by weighing approximately 3 grams of the Fischer-Tropsch samples into a centrifuge tube, adding 3-5 ml of toluene, shaking until the total sample was dispersed, and then centrifuging for five minutes. The supernatant liquid was removed and filtered over a pre-weighed 4-5.5 micron frit. This procedure was repeated until the extracting toluene was clear (usually 3-4 extractions). Finally, the remaining insoluble wax was transferred quantitatively to the frit which upon drying was reweighed to calculate percent insoluble wax. The toluene solution containing the extracted hydrocarbons and oxygenates was reconcentrated to obtain a 3 ml solution which was injected onto the LC column described above. The injected sample was eluted sequentially with hexane (250 ml), methylene chloride (250 ml), and methanol (150 ml) at flow rates of 5-6 ml/min. The solvents were removed with a three ball Snyder column and modified nitrogen purged pre-weighed beakers. After solvent evaporation the beakers were re-weighed to obtain a weight percent analysis on each LC fraction (Table 1). 99.6% of the total sample injected onto the silica column was recovered. Samples containing residual C5-C9 hydrocarbons may exhibit lower recoveries due to the loss of these hydrocarbons during solvent evaporation.

Argentation Liquid Chromatography. A 30 cm x 9 mm i.d. glass column was packed with 20% silver nitrate impregnated on 32-63 micron Woelm silica gel (12). The silica was prepared by dissolving the silver nitrate in acetonitrile and then adding the silica. The solvent was removed in a dark room by rotary evaporation while purging with nitrogen and heating with an infra-red lamp. The packed glass column was protected from light by completely covering with aluminum foil.

The capacity of the silver nitrate column was approximately 100 mg of total hydrocarbons isolated from the silica column. Three separate injections were made for each sample.

Gas Chromatography. Gas chromatographic analysis on each LC fraction was performed on a SIGMA 2 GC (Perkin Elmer, Norwalk, Ct.) equipped with a flame ionization detector. OV-101 Glass SCOT columns were purchased from SGE (Austin, Texas). Samples were injected in the splitless mode.

A packed 6' x 1/8" SS 1.5% Dexsil 300GC on Supelcoport (Supelco, Bellefonte, Pa.) column was used for the paraffin fraction. Peak integration was performed with a Varian 620 Data System.

RESULTS/DISCUSSION

Major Functional Groups. IR spectra of the three Fischer-Tropsch samples prior to liquid chromatographic analysis are given in Figure 2. The major absorption bands of interest are the carbonyl (1700-1750 cm^{-1}), olefin (910 cm^{-1}, 955 cm^{-1}) and the $(CH_2)_x$ (1720-730cm^{-1}). The carbonyl bands for all three samples indicate the presence of more than one carbonyl functional group. In Sample A α-olefins (910 cm^{-1}) predominate; however, sample B has approximately equal amounts of α-(910 cm^{-1}) and β-olefins (960cm^{-1}) while in sample C the β-olefins are the major olefins.

The bands at 720-730 cm^{-1} which are characteristic to long chain paraffins are proportional to the high molecular weight wax present. Samples B and C exhibit a strong absorption due to the high content of insoluble wax present in these samples. Sample A which contained no detectable insoluble wax has a low absorption at 720-730 cm^{-1}.

Paraffins. Gas chromatographic fingerprints (Figure 3) of the paraffins isolated by argentation LC indicate that Samples B and C contain normal paraffins up to approximately C45. In contrast, Sample A contains normal paraffins up to approximately C35. In addition, the latter sample contains a distinct second maximum at C21-C22 and a relatively large envelope. Components appearing between the normal-paraffins (Figure 3) are believed to be iso-paraffins (13,14).

Olefins. Gas chromatograms of the three olefinic fractions isolated by argentation LC are shown in Figure 4. The two major olefin types observed in all samples are the linear α-olefin and the β-olefin. In Sample A the linear α-olefins are the major components whereas in Sample B both the linear α- and β-olefins predominate. In Sample C linear β-olefins are the major components. These results are consistent with the IR data presented in Figure 2.

Other minor olefins believed to be methyl-substituted are also present. In all three samples olefins were detected up to C22-C25.

Ketones and Esters. Infra-red analysis of the methylene chloride LC fraction (Figure 5) indicated that the major functional groups were ketones (1705 cm^{-1}) and esters (1735 cm^{-1}). The aldehyde content is very low as evidenced by the lack of significant absorption at 2720-2820 cm^{-1}. No aldehydes were detected by FT H-NMR. In addition to IR analysis these compound classes were confirmed by wet chemical functional group micro-reaction. Gas chromatograms were compared before and after reaction and the shifting and/or decrease in peak areas indicated a positive reaction. Esters were confirmed by reaction with methanolic-sodium hydroxide and ketones by reaction with 2,4-dinitrophenylhydrazine (15). Individual components were identified by co-injection with authentic standards. Figure 6 compares the SCOT column chromatograms of Samples A and C methylene chloride fraction. Sample B produced a gas chromatogram similar to that of Sample C.

Methylketones are the major components in all three samples. This was confirmed by gas chromatography and FT H-NMR and C13-NMR. Sample A contains detectable esters which were confirmed by the methanolic-sodium hydroxide reaction.

Alcohols and Acids. IR analysis of the methanol LC fraction (Figure 5) indicated the presence of alcohol (3420 cm^{-1}) and carbonyl (1705 cm^{-1}) bands. The carbonyl band was attributed to carboxylic acids as confirmed by a separate extraction of the total sample with aqueous $NaHCO_3$ (Figure 5). No methylketone contamination from the methylene chloride fraction was detected by gas chromatography.

The alcohols in this fraction were confirmed by gas chromatography by acetylating with acetic anhydride in the presence of pyridine (16) which resulted in peak shifting and improved peak efficiency (Figure 7). Individual components were identified by co-injection with standard compounds. Sample A alcohols (Figure 7a) consisted mostly of normal alcohols up to C20 whereas Sample B contained both normal and secondary alcohols which paralleled the linear α- and β-olefin concentration (Figure 4C). Sample C contained only trace amounts of alcohols. Initial studies of the methyl derivatives of the extracted acids indicated that normal-carboxylic acids of C5 to C10+ are present in these samples.

Carbon Number Distribution Plots. Distribution plots for two of the three samples were reconstructed for the major components of various functional groups (Figures 8 and 9). Oxygenates, having boiling points higher than their corresponding hydrocarbons of the same carbon number reached a maximum at lower carbon numbers. This maximum may vary depending on the exact boiling point cut of the Fischer-Tropsch sample.

Distribution plots of oxygenates (methylketones, n-carboxylic acids and alcohols) follow closely those of the linear α-olefins and β-olefins. The ratio of linear α-olefins to β-olefins is strongly dependent on process conditions (e.g. temperature). Both the olefins and the oxygenates contain detectable carbon numbers up to approximately C22-C25.

Except for the linear α-olefins and alcohols the other products are probably formed in secondary reactions (14). Of interest is the carbon number distribution plot for the major esters detected in Sample A (Figure 8) which exhibits a maximum at higher carbon number than the other oxygenates. These esters are believed to be mixed esters as a result of secondary reactions occurring in the reactors among the major carboxylic acids and the major alcohols present:

$$R_1\overset{O}{\overset{\|}{C}}\text{-OH} + R_2\text{-OH} \longrightarrow R_1\overset{O}{\overset{\|}{C}}\text{-OR}_2$$

$$(R_1 = n,\ n+1,\ n+2\ \ldots) \qquad (R_2 = m,\ m+1,\ m+2\ \ldots)$$

CONCLUSION

Chromatographic techniques have been developed which will allow a detailed characterization of Fischer-Tropsch high boiling hydrocarbons and oxygenates obtained under various process conditions. These techniques are currently being refined to include newer chromatographic techniques (e.g. fused silica capillary columns-GC, GC/FT-IR) and mass spectrometric characterization of the minor and major components.

ACKNOWLEDGMENTS

The author wishes to thank S. J. Lucki, J. A. Brennan and J. Kuo for kindly providing the Fischer-Tropsch samples, and J. G. Ehlers and M. E. Landis for obtaining the IR and NMR data. Permission granted by Mobil Research/Development Corp. to publish the results of this study is also appreciated.

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TABLE 1

LIQUID CHROMATOGRAPHIC ANALYSIS OF 170°C+ COMPONENTS

	SAMPLE A	SAMPLE B	SAMPLE C
Paraffins	72.7	70.4	78.4
Olefins	16.2	13.2	9.4
Esters + Ketones	10.6	1.5	6.3
Acids + Alcohols	1.1	2.0	0.2
Insoluble Wax	0	12.5	5.7
Loss	0.4	0.4	0.4

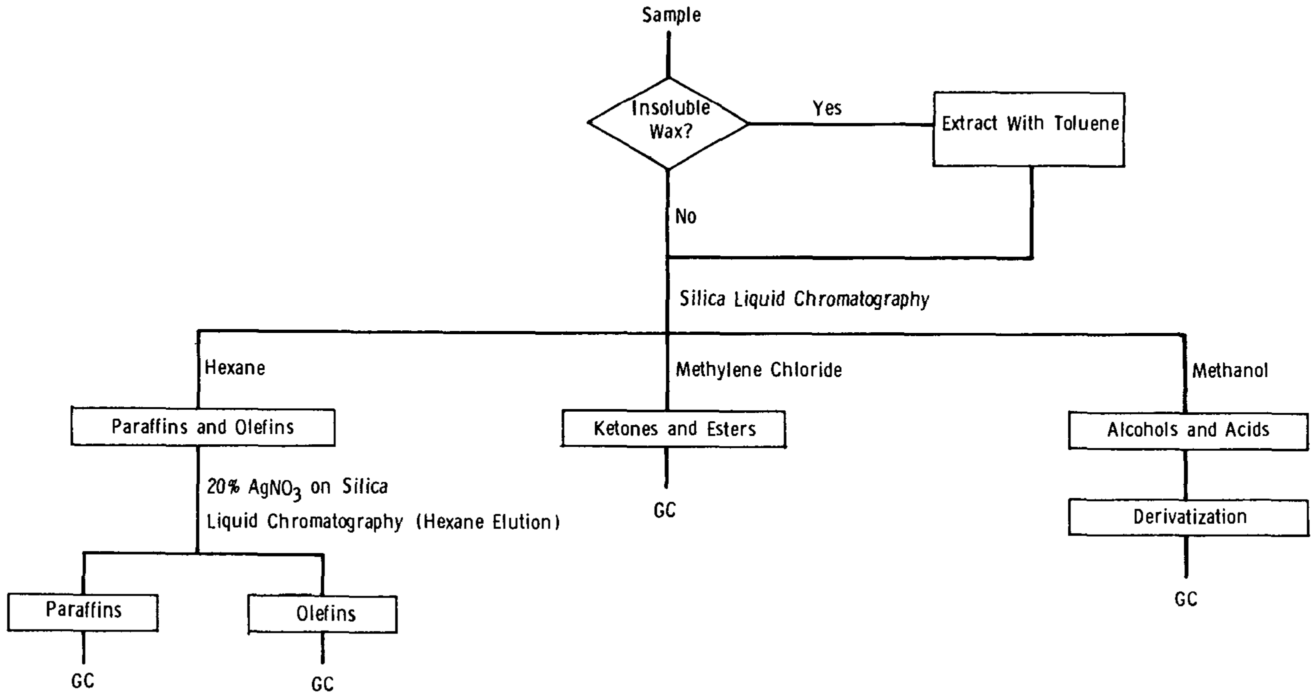

FIGURE 1: SEPARATION SCHEME FOR FISCHER-TROPSCH MATERIALS

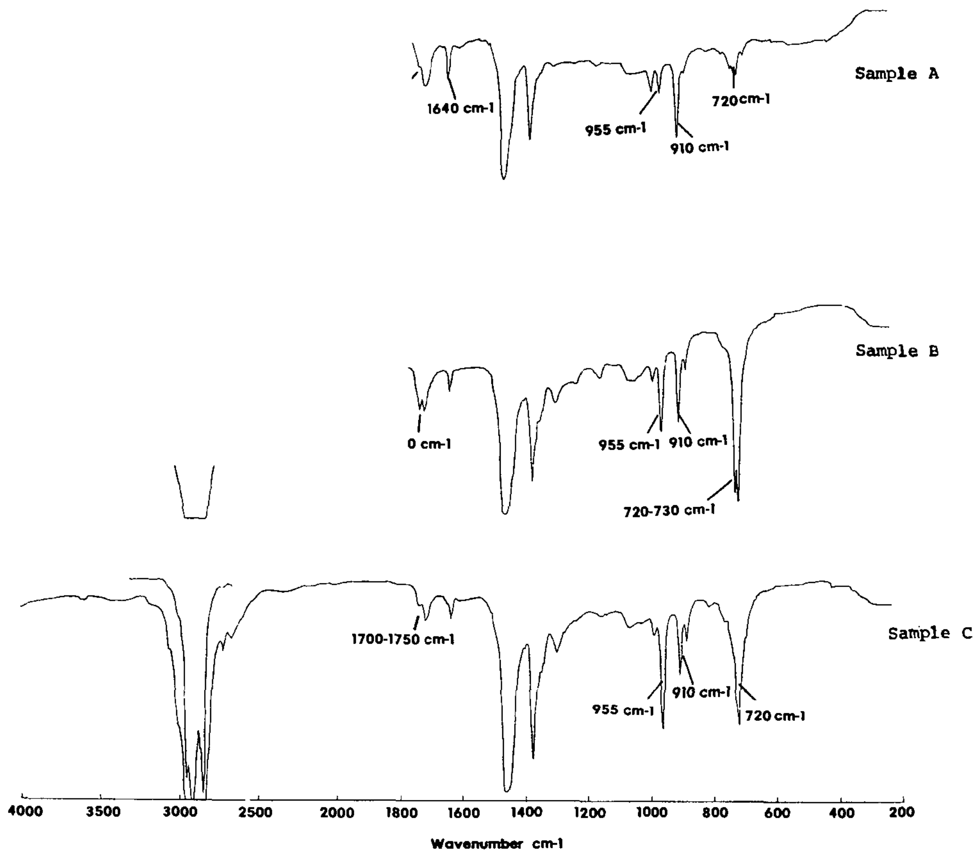

FIGURE 2: IR SPECTRA OF FISCHER-TROPSCH MATERIALS PRIOR TO LC FRACTIONATION

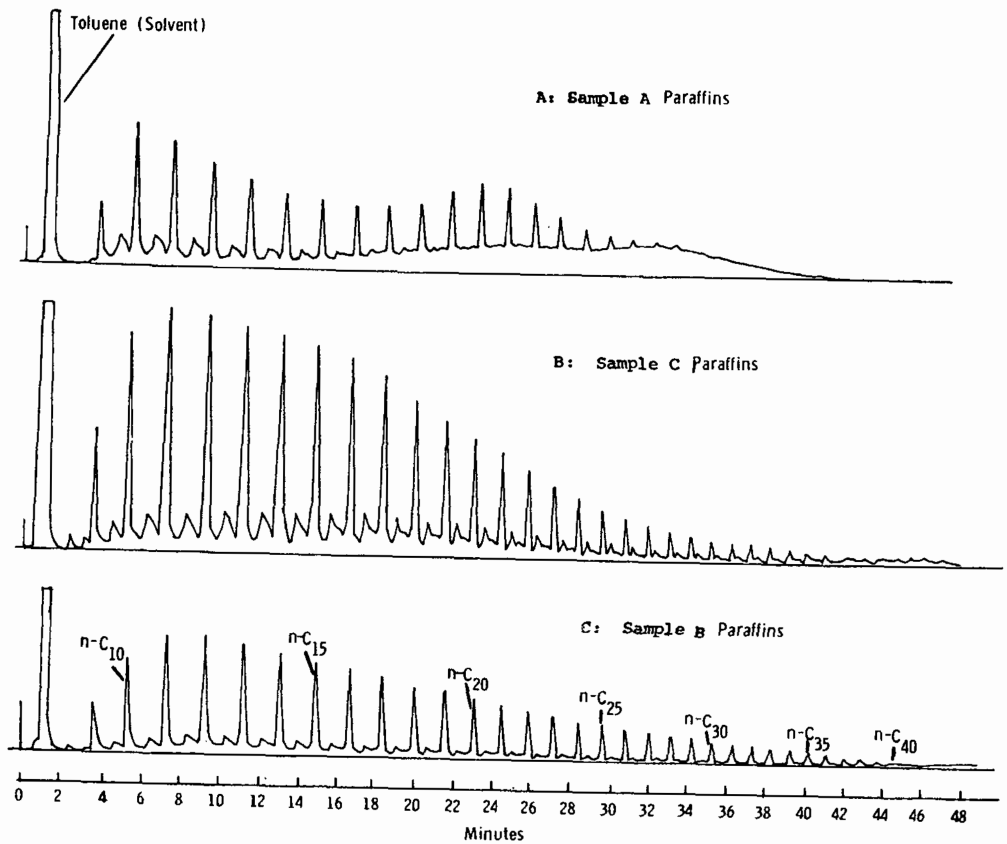

FIGURE 3: PACKED COLUMN GAS CHROMATROGRAMS OF PARAFFINS FROM ARGENTATION LC

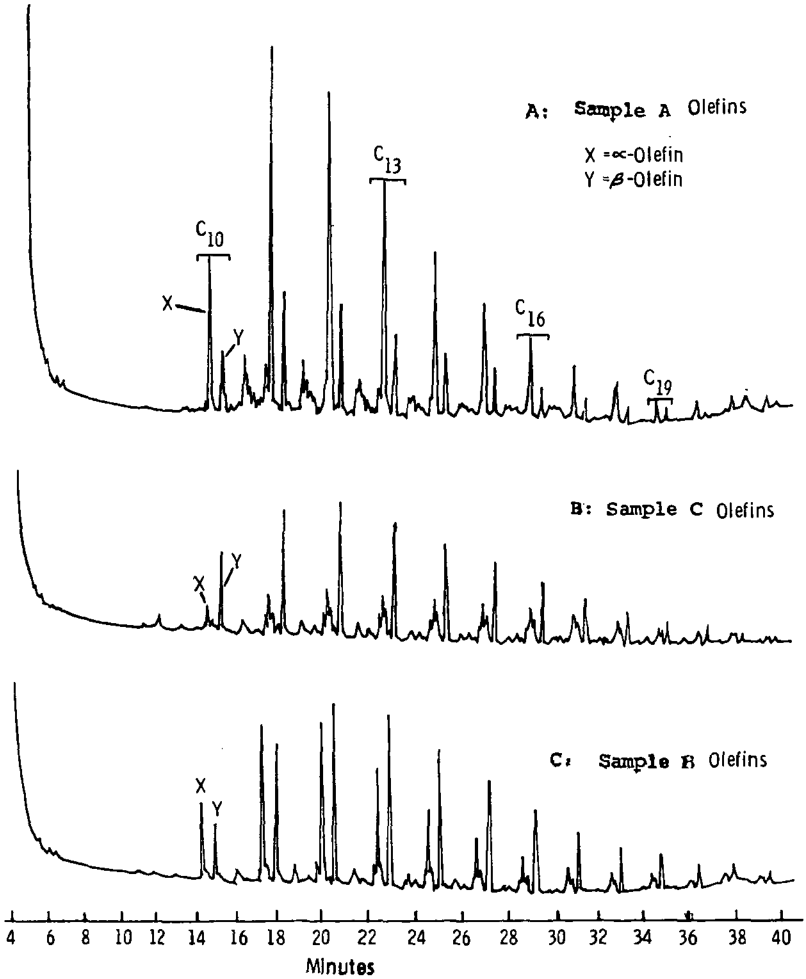

FIGURE 4: OV-101 SCOT COLUMN GAS CHROMATOGRAMS OF OLEFINS FROM ARGENTATION LC

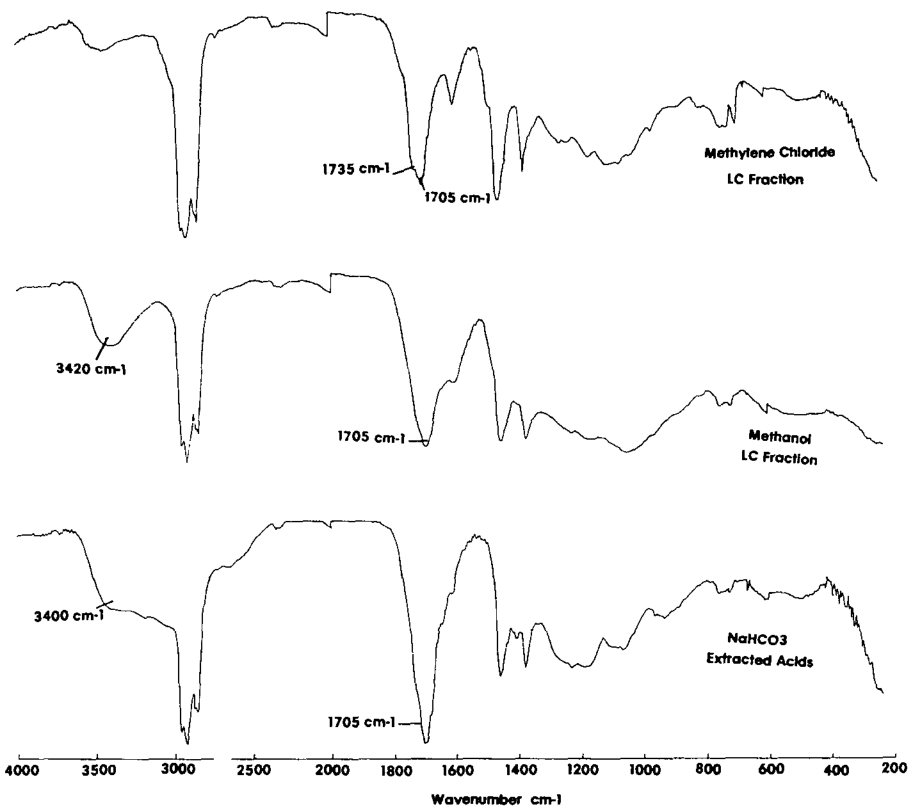

FIGURE 5: SAMPLE A METHYLENE CHLORIDE-METHANOL LC FRACTIONS AND $NaHCO_3$ EXTRACTED ACIDS

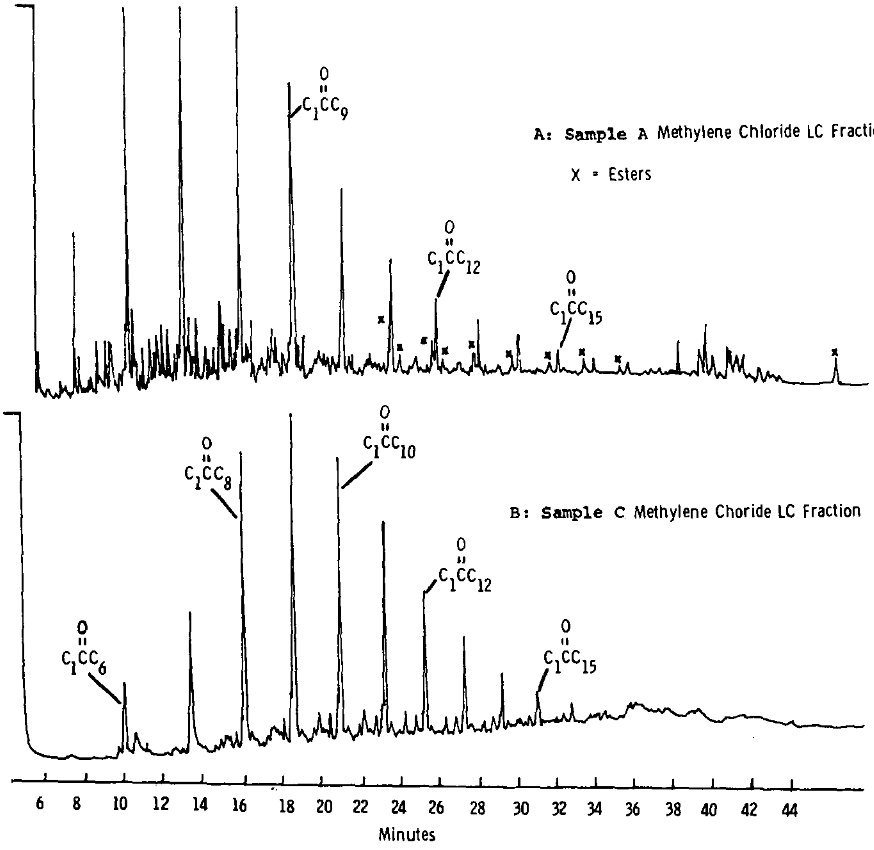

FIGURE 6: OV-101 SCOT COLUMN GAS CHROMATOGRAMS OF SAMPLE A AND SAMPLE C METHYLENE CHLORIDE LC FRACTIONS

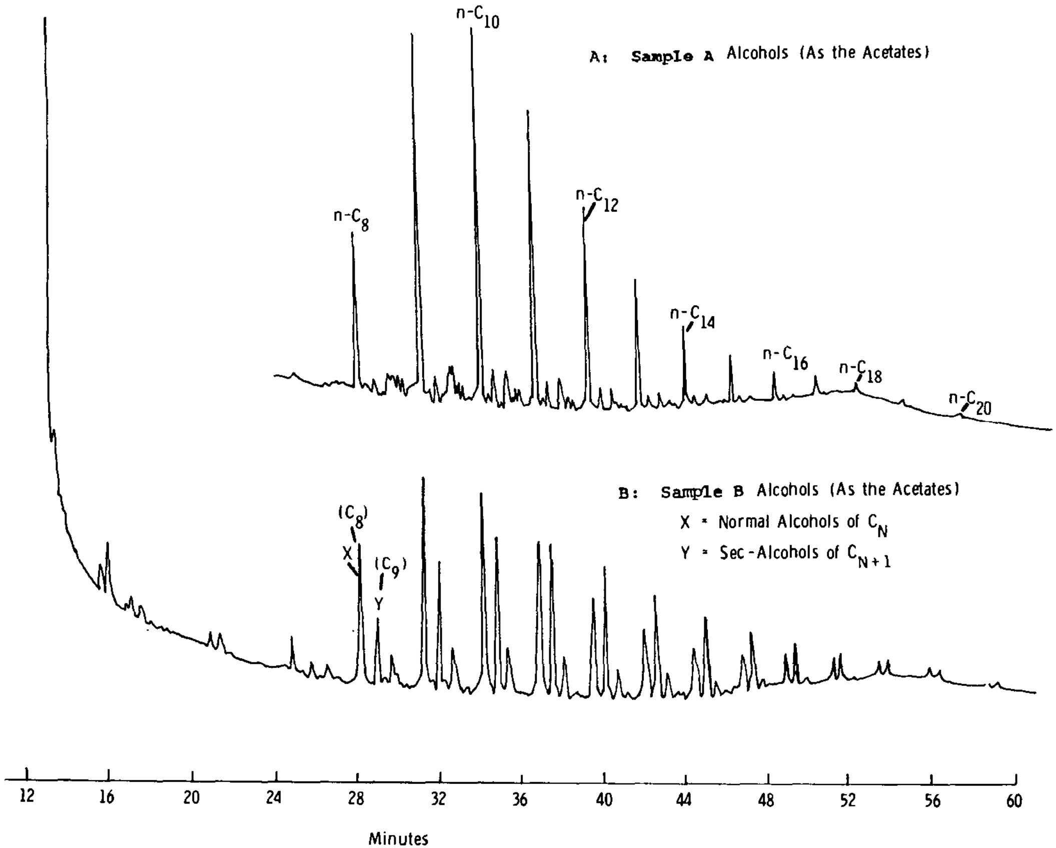

FIGURE 7: OV-101 SCOT COLUMN GAS CHROMATOGRAMS OF ALCOHOLS PRESENT IN THE METHANOL LC FRACTIONS

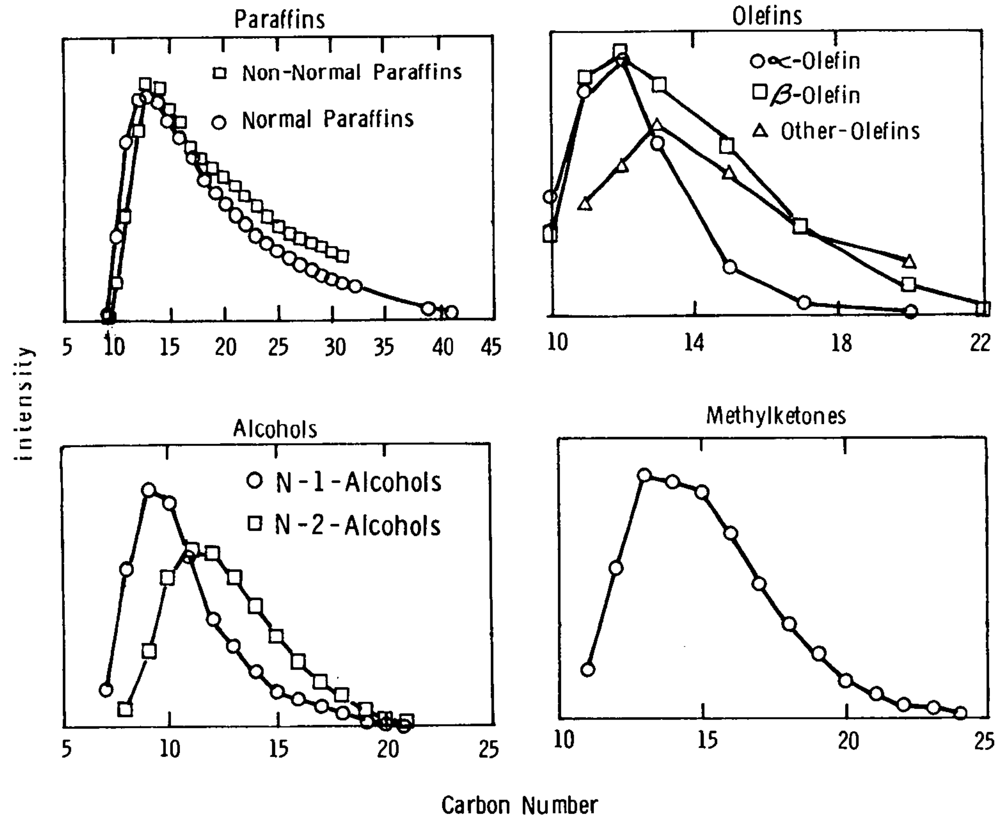

FIGURE 8: CARBON NUMBER DISTRIBUTION PLOTS: SAMPLE B

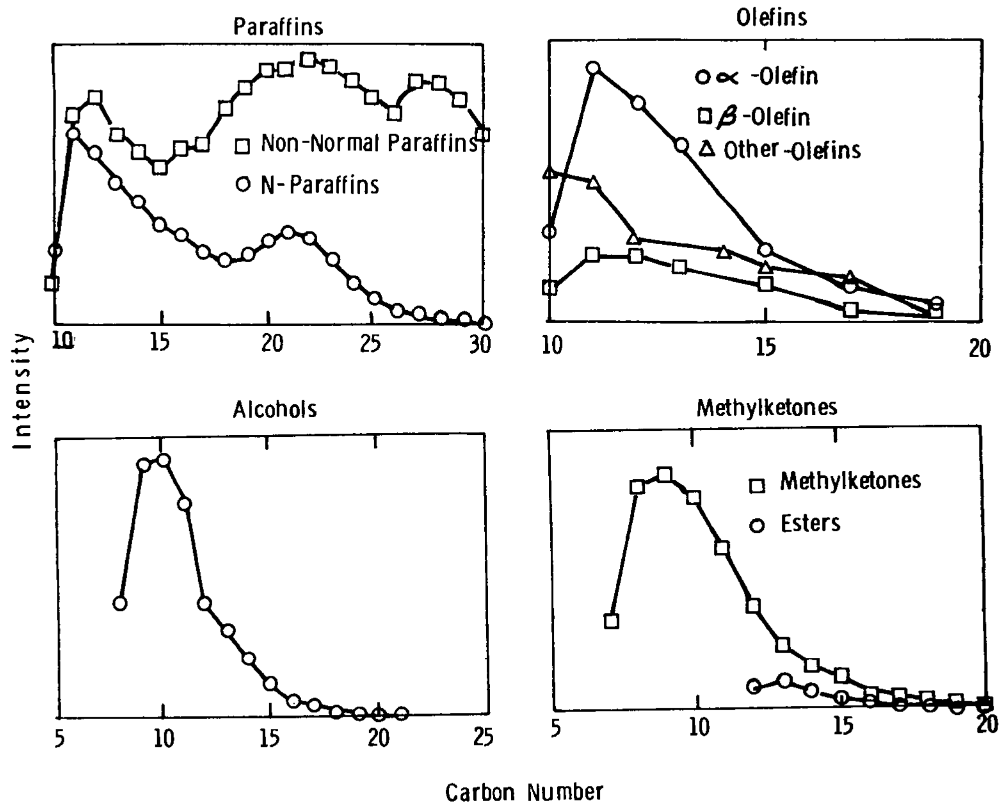

FIGURE 9: CARBON NUMBER DISTRIBUTION PLOTS: SAMPLE A